This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

CHEM. LIB.
QD
115
.H642

B 453598

The
Determination of Anions
in the
Electrolytic Way

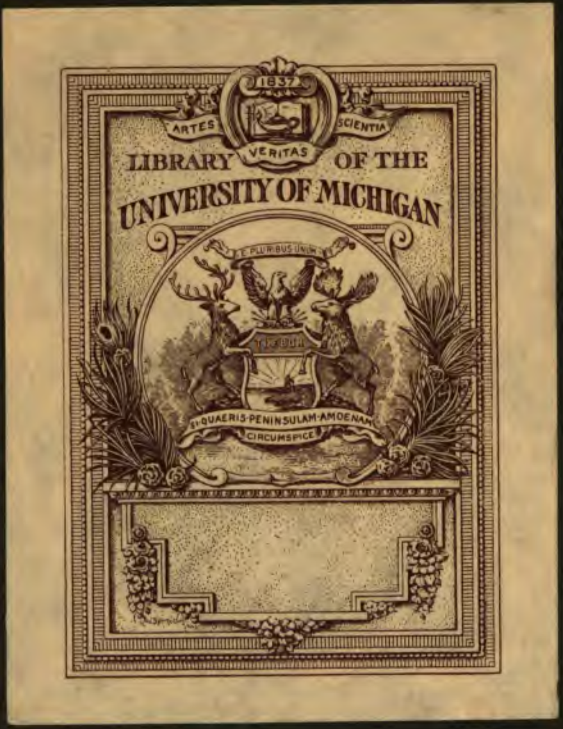
THESIS

PRESENTED TO THE FACULTY OF THE DEPARTMENT OF
PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

BY

JOEL HENRY HILDEBRAND,

WAYNE, PA.


1837
ARTES
VERITAS
SCIENTIA
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
E PLURIBUS UNUM
TUEBOR
SI QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE

U of M
Received
Sep 26, 1906

Chemical Library
QD
115
.H642

The
Determination of Anions
in the
Electrolytic Way

THESIS

PRESENTED TO THE FACULTY OF THE DEPARTMENT OF
PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

BY

JOEL HENRY HILDEBRAND,
WAYNE, PA.

1906

THE JOHN C. WINSTON CO.
1006-1016 ARCH STREET
PHILADELPHIA, PA.

The Determination of Anions in the Electrolytic Way

INTRODUCTION

The electrolytic determination of metals was begun in 1865. The procedure has in the intervening years been applied to nearly all metals with the greatest success in most cases, particularly since there has been added the rotating anode (Exner, 1903) whereby the time factor has been reduced to such a degree that electrolytic methods are now vastly superior in every way to the ordinary gravimetric procedures. The negative groups in salts—the anions—have in the period of metal determination received scant attention from the electro-analyst. The few observations of Vortmann[1] and Specketer[2] have attracted little attention, and only since Smith[3] by the use of a mercury cathode and a silver anode made successful estimation simultaneously of both components in sodium chloride, barium chloride, strontium bromide, etc., has the idea of estimating anions electrolytically become a subject of serious thought. The experiments of Withrow (thesis 1905) were directed to this end. They, however, showed that ultimate and most complete success would probably come only by the use of the combined anode and mercury cathode. The present investigation was begun with this thought constantly in mind. The results when studied will clearly prove that it is now possible to determine not only halogens, but even anions such as CO_3, CNS, $Fe(CN)_6$

---

[1] Monat. f. Chem., **15**, 280; **16**, 674. Elec. Chem. Zeit. (1894), I 137. Akad. d. Wissenschaft. Wein., **11**, 7, 95.

[2] Zeit. Elec. Chem. **4**, 539.

[3] Jr. Am. Ch Soc **25**, ~~[illegible]~~.
883, (1903)

151107

and others. Salts that are analyzed with difficulty by time honored methods are now electrolyzed most easily and with exceeding accuracy in exceedingly short periods of time. That separations of anions will also be made in the same manner appears certain of realization, although this present research has been restricted to their determination alone, and to the perfection of the apparatus necessary for that purpose.

RESULTS WITH STATIONARY ANODE.

Apparatus. The mercury cathode cell as described by Myers[1] was used to contain the solution to be electrolyzed. As anodes there were three platinum gauzes 5 by 10 cm. attached to stiff platinum wires and rolled into cylinders with the shorter dimension as axis and of such diameter as to be suspended readily in the cell. These gauzes were plated with silver from a double cyanide electrolyte the coating being made as heavy as possible. After washing with water, alcohol and ether, the deposits were carefully brushed with a soft camel's hair brush to remove all loosely adherent silver and then weighed, being suspended by a hook bent into the top of the wire support.

Method of Procedure.—The chief difficulty, as with previous workers, was that of determining the end of the decomposition. In spite of the greatest care in keeping the mercury and the interior of the cell absolutely clean in order to minimize the secondary decomposition of the amalgam, the formation of some caustic could never be entirely prevented, and after the salt was all decomposed the weight of the gauze could be further increased indefinitely by the formation of silver oxide from the electrolysis of the caustic. Various schemes were tried to determine the end of the decomposition, the one finally serving the purpose being as follows:

At the beginning of the operation the gauze was suspended within about 5 mm. of the surface of the mercury and the liquid diluted so as to cover only about one-third of the gauze. During the electrolysis the potential was kept constant, then the strength of the current falling as the action progressed indicated the completeness of the decomposition. The current was only prevented from falling to zero by the slight amount of caustic formed. When it had reached a minimum,—usually from 0.005 to 0.02 amperes,—the level of the liquid was raised a few millimeters from time to time, and as soon as the fresh surface showed the formation of brown silver oxide—which could easily be distinguished from the bluish black chloride—the gauze was removed, immersed in alcohol, then in ether, dried and weighed. By this method it was possible to obtain consecutive concordant results. In each case the amalgam was washed into a beaker and after it had decomposed the alkali was titrated with tenth normal sulphuric acid with methyl orange indicator.

---

[1] Jr. Am. Ch. Soc. 26; 1124.

SODIUM CHLORIDE.

The following table gives the results obtained for sodium chloride. The current in amperes at the beginning and end of each decomposition is given in the third column.

Time, minutes.	Volts.	Amperes.	Sodium in grams. Present.	Sodium in grams. Found.	Chlorine in grams. Present.	Chlorine in grams. Found.
135	3.5	.08–.01	0.0460	0.0461	0.0708	0.0713
210	3.5	.09–.003	0.0460	0.0456	0.0708	0.0706
150	3.5	.20–.005	0.0460	0.0460	0.0708	0.0706
220	3.5	.24–.005	0.0460	0.0458	0.0708	0.0705
200	3.5	.21–.005	0.0460	0.0462	0.0708	0.0709
120	3.5	.16–.01	0.0460	0.0459	0.0708	0.0712
130	3.5	.20–.02	0.0460	0.0461	0.0708	0.0705
70	3.5	.15–.04	0.0460	0.0459	0.0708	0.0707
	3.5	.14–.03	0.0460	0.0463	0.0708	0.0711
	3.5	.13–.02	0.0460	0.0463	0.0708	0.0710

The deposits were always perfectly adherent in character unless the silver coating was too thin. No attempt was made to protect it from the light, so that the deposits both here and with other substances were always very dark colored; in fact, with several other salts if the silver salt was formed so rapidly as to show its true color at places, it was often not very adherent.

SODIUM BROMIDE.

The same procedure as with the chloride was immediately successful in this case.

Time. minutes.	Volts.	Amperes.	Sodium in grams.		Bromine in grams.	
			Present	Found.	Present.	Found.
60	4·0–3·5	.13–.02	.0232	.0235	.0804	.0794
45	4·0–3·5	.15–.05	.0232	.0237	.0804	.0806
50	3·5	.12–.03	.0232	.0231	.0804	.0806
100	3·5	.13–.01	.0232	.0237	.0804	.0812
60	3·5	.12–.05	.0232	.0238	.0804	.0804
	3·5	.09–	.0232	.0230	.0804	.0805

SODIUM IODIDE.

Equally satisfactory results were obtained with this salt.

Time. minutes.	Volts.	Amperes.	Sodium in grams.		Iodine in grams.	
			Present.	Found.	Present.	Found.
70	4–3·5	.10–.02	.0154	.0156	.0850	.0850
70	3·5	.05–.01	.0154	.0156	.0850	.0857
45	3·5–3	.10–.02	.0154	.0154	.0850	.0845
75	3	.07–.01	.0154	.0157	.0850	.0846
60	4–3·5	.08–.02	.0154	.0156	.0850	.0855
60	3·5	.08–.02	.0154	.0156	.0850	.0852

POTASSIUM SULPHOCYANIDE.

This salt proved more troublesome as the potassium amalgam usually started to decompose rapidly near the end of the electrolysis.

Time. minutes.	Volts.	Amperes.	Potassium in grams.		CNS in grams.	
			Present.	Found.	Present.	Found.
45	3·5	.10–.06	.0375	.0371	.0558	.0558
120	3·5	.07–.04	.0375	.0379	.0558	.0560
105	4–3·5	.10–.01	.0375	.0379	.0558	.0560
135	3·5	.06–.01	.0375	.0375	.0558	.0566
65	4–3·5	.09–.01	.0375	.0373	.0558	.0553

It was soon after found that there could be formed silver ferro- and ferri-cyanides and, what seemed still more remarkable, silver carbonate. In the last instance the decomposition was complete, there being no traces of carbon dioxide liberated at the anode. The deposit afterwards immersed in dilute sulphuric acid liberated carbon dioxide with effervescence. However it was impossible to make these depositions quantitative as the silver salts formed were not very coherent and at the edge of the gauze near the mercury, where the deposit was thick, part of it always became detached. It was then thought that perhaps this difficulty could be overcome by using an anode in which the gauze was horizontal thus presenting a uniform surface over which the deposit might be distributed, and at the same time decreasing the resistance so that the decomposition might be more rapid.

Anode.—The anode devised consisted of two circular disks of platinum gauze 5 cm. in diameter and having 300 meshes per sq. cm. The circumference was slightly fused in the blowpipe. These were mounted 5 mm. apart on a stout platinum wire 1 mm. in diameter and 10 cm. long which passed through the centers of the disks perpendicular to them. Each disk was attached to this axial wire by means of two smaller wires fitting tightly into two adjacent holes drilled at right-angles to each other through the large wire. Two such anodes were made by the Bishop Platinum Co., Malvern, Pa. weighing about 16 grams apiece. They would have been improved slightly if the axial wire had not protruded below the lower gauze. The total surface of each pair of disks is about 100 sq. cm. which is at least doubled when coated with several grams of silver. Since it requires only about 30 cc. of liquid to cover the disks as against 150 cc. for a platinum disk of equal surface it will be interesting to determine how it will compare with the usual platinum dish as a cathode for rapid deposition of metals, as well as an anode for lead and manganese peroxides. This will shortly be done in this laboratory. This electrode has the further advantages over the dish in the ease with which it may be washed and in its light weight. These anodes were always supported when not in use by fastening the axis in a clamp so that the gauze might not come in contact with anything which might bend it. In order to suspend them from the balance beam in weighing, a loop of fine platinum wire was soldered to each axial wire about 2 cm. from the top.

Silver plating the anodes.—In plating the anodes with silver the rotator was always used, as a coating of 3 to 4 grams of silver could thus be deposited. A number of determinations could then be made without replating the gauze, the deposited silver being merely dissolved off by immersing for a few moments in potassium cyanide, thus exposing a fresh surface of silver. The plating was done in a beaker, the anode being a platinum wire passing through a glass tube to the bottom of the beaker where it was bent into a flat horizontal spiral. A strong stock solution of silver potassium cyanide was kept in a bottle and portions added to the beaker from time to time as the silver in the electrolyte was deposited. No particular care is necessary in this plating as the conditions may be varied rather widely without injuring the deposit; about 5 volts and 1 to 2 amperes were the ordinary conditions. When the coating was sufficiently heavy the gauze was removed, washed by immersing in distilled water, followed by alcohol and ether. In the later work the alcohol and ether washing was omitted and the gauze dried by suspending for a short time over a steam radiator.

To avoid the necessity of centering the anode each time it was placed in the rotator, a small piece of copper foil was rolled into a cylinder about the axis of the anode and then put permanently into the tip of the rotator. The anode was thus always centered when put in position.

The cell.—This anode was first tried with sodium chloride, the cell being a beaker of diameter slightly greater than that of the anode. Since it is difficult to fuse a platinum wire into a vessel of this size, connection was made with the mercury by means of a platinum wire fused through the closed end of a glass tube. Into this tube was put a little solder which was heated and then while molten, a stout copper wire was thrust into it. This tube was clamped so that it lay close to the side of the beaker, the platinum wire at the tip projecting into the mercury.

With this arrangement it was found that while the electrolysis was more rapid, the greater surface of mercury exposed to the liquid favored the decomposition of the amalgam to an extent inconsistent with good results. A method was therefore sought to dispose of the amalgam and prevent the presence of alkali about the anode. After much experimenting a cell was devised which answers the purpose admirably. In principle it resembles the Castner-Kellner process for caustic soda, the amalgam being formed in one compartment and decomposed in another. The outer cell is a crystallizing dish 11 cm. in diameter and 5 cm. deep. Inside of this is a beaker 6 cm. in diameter with the bottom cut off and the edge rounded so that a ring is formed 4.5 cm. high. This rests on a large Y of thin glass rod on the bottom of the crystallizing dish and is kept in position by three rubber stoppers fitting radially between it and the inside of the dish. In the outer compartment thus formed there is a ring of about six turns of nickel wire provided with three legs which are fastened to the ends of the glass Y and serve to support the ring about 1 cm. above the surface of the mercury when sufficient of the latter is poured in to seal off the two compartments. The cell and anode are shown in Fig. 1.

In using this cell, which must be kept scrupulously clean, pure clean mercury is poured in so that its level is about 3 mm. above the lower edge of the bottomless beaker. The solution to be electrolyzed is then put into the inner compartment; into the outer is placed enough distilled water to cover the nickel wire, and to this is added a few cc. of a saturated solution of common salt. By this arrangement the amalgam formed in the inner compartment is immediately decomposed in the outer, which acts as a cell whose elements are amalgam-sodium chloride-nickel wire. The sodium chloride serves merely to make the liquid conducting so that the action may proceed more rapidly at the beginning. Without this scheme the amalgam is not entirely decomposed in the outer compartment as pure water does not attack it rapidly enough to prevent a partial decomposition in the inside cell. The mercury is connected with the negative pole of the battery by means of the glass tube bearing the copper and platinum wires described above, which dips into the outer compartment. After the electrolysis is complete the entire contents of the cell are poured into a beaker, the cell rinsed and the alkali titrated. After titration the mercury is washed, the water decanted,

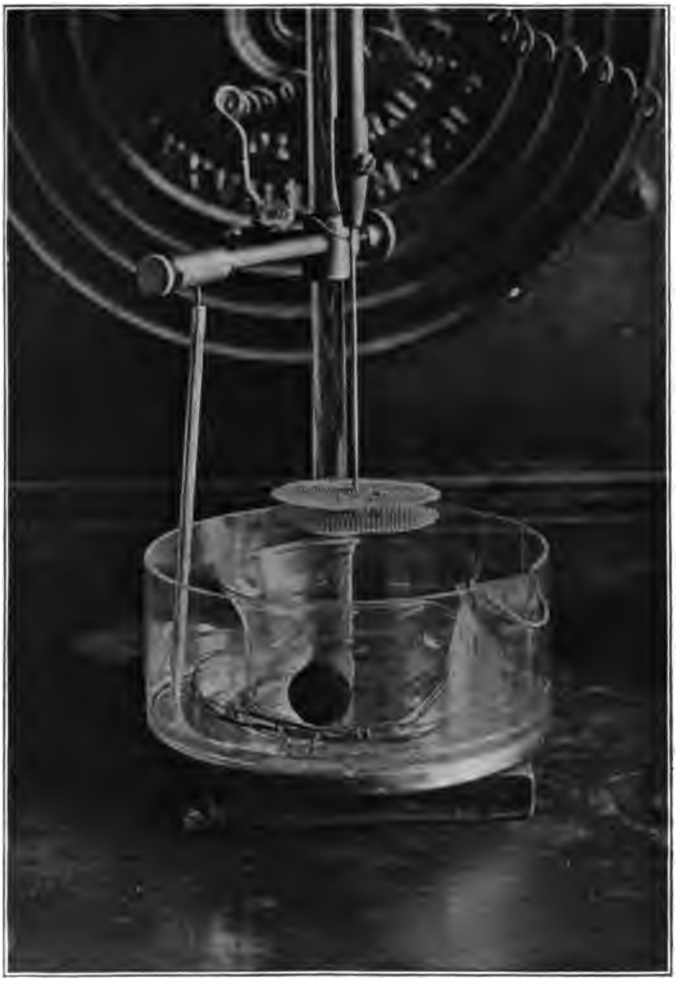


FIG. 1.

and the metal poured into a large separatory funnel from which it can be drawn off clean and dry.

SODIUM CHLORIDE.

This apparatus was first tried on sodium chloride, the anode being stationary, with the following results.

Time, minutes.	Volts.	Amperes.	Sodium in grams.		Chlorine in grams.	
			Present.	Found.	Present.	Found.
30	4.0–2.5	.50–.02	.0461	.0459	.0708	.0704
45	3.5–2.5	.34–.01	.0461	—	.0708	.0706
40	3.5–3.0	.50–.01	.0461	—	.0708	.0704
45	4.0–3.5	.65–.01	.0461	—	.0708	.0716
30	4.0–2.5	.76–.02	.0461	—	.0708	.0713
55	3.0	.26–.02	.0461	—	.0708	.0709

These results are given merely for completeness as sodium chloride was not tried again although the use of the rotator, as in the following work, would certainly give better results, for on account of the lack of any stirring of the amalgam there was still a very slight decomposition on the inside.

RESULTS WITH ROTATING ANODE.

When it was found that the bromide did not adhere completely to the anode when stationary the rotator was tried and gave the double advantage of making the deposit perfectly adherent and stirring the amalgam so that it was completely decomposed in the outer compartment. When the electrolysis was complete therefore nothing but pure water remained so that the current falling to .01 ampere or less indicated the end, and no harm could be done by running too long as no further increase in weight was possible.

In using the rotator the weighed gauze is clamped in the shaft which is then lowered into the cell till the lower gauze is about 5 mm from the surface of the mercury. The motor and belt are adjusted, the motor started and the electrolyzing current turned on. About 300 revolutions per minute is the best speed for the motor. Fig. 2 shows the entire apparatus.

The variation in current as the electrolysis proceeds is shown by the curve in Fig. 3 and the rate of decomposition calculated from it in Fig 4.

It is not necessary to wash the anode after the salt is deposited as the water remaining is pure. This avoids any possibility of loss by the usual washing in water, alcohol and ether, although the latter two may be used where it is desire

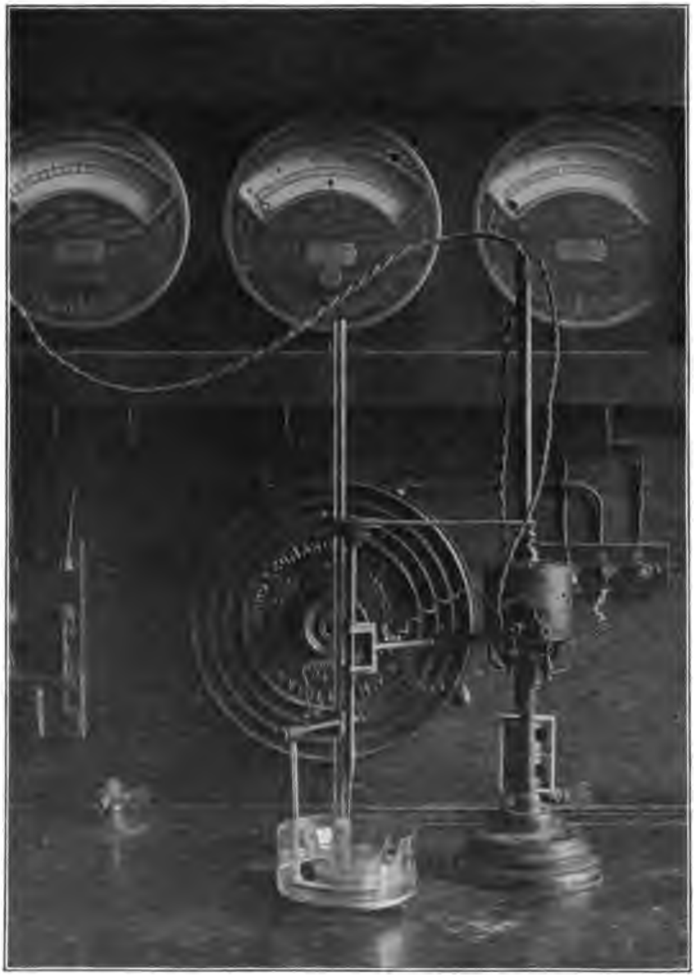


Fig. 2.

still further to reduce the time. The writer is accustomed to suspend the gauze over a steam radiator whereby it is dry in about fifteen minutes.

SODIUM BROMIDE.

This salt gave the following results with the rotator.

Time, minutes.	Volts.	Amperes.	Sodium in grams. Present.	Sodium in grams. Found.	Bromine in grams. Present	Bromine in grams. Found.
30	5.0	.65–.01	.0231	.0233	.0800	.0798
30	5.0	.65–.01	.0231	.0233	.0800	.0802

In this case a dilution of about 25 cc. was used, it being necessary to cover only the lower gauze, as this gave sufficient surface for the quantity of sodium bromide used.

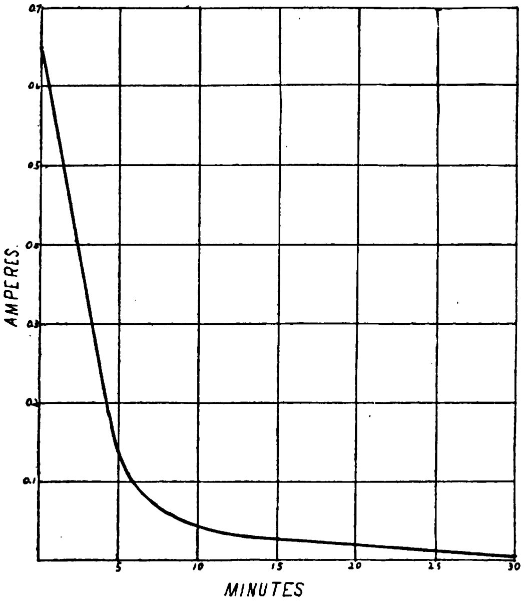


FIG. 3.

SODIUM CARBONATE.

Sodium carbonate required a little more care, it being found advantageous to deposit the carbonic acid a little slower, and also to use a slightly roughened silver surface obtained by stopping the rotator several minutes before taking the gauze from the silver plating bath. Furthermore, towards the end